Supporting information

Unveiling the Zwitterionic Nature of Ethyl Piperazine-based Dithiocarbamate Chain Transferring Agent for Achieving High Molar Mass of Poly Vinyl Acetate: Experimental and Computational Insight

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Table S1. Results for the homo-polymerization of VAC by using CTA-1 at a fixed concentration (500:1:0.1).

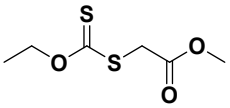
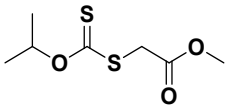
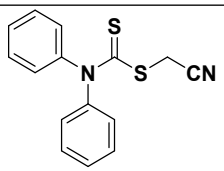
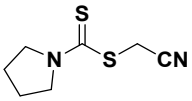
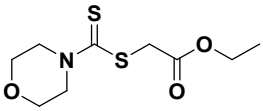
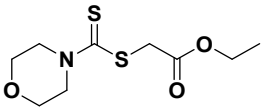
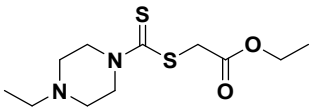
Entry	M: CTA: I	Time(min)	Conversions (%)	$M_{n,THEO}$ (Da)	$M_{n,SEC}$ (Da)	*Đ*
1	500:1:0.1	15	23	10170	5340	1.21
2	500:1:0.1	30	42	18340	7590	1.17
3	500:1:0.1	45	63	27380	9890	1.15
4	500:1:0.1	60	80	34400	13240	1.11
5	500:1:0.1	90	95	40870	16400	1.12

Table S2. Kinetic study for the homo-polymerization of VAc by using CTA-1, -2 and without CTA at a fixed concentration (500:1:0.1).

Entry	M: CTA: I	Time(min)	CTA-1 (%)*	CTA-2 (%)*	Without CTA* (%)
1	500:1:0.1	15	23	19	65
2	500:1:0.1	30	42	36	90
3	500:1:0.1	45	63	41	93
4	500:1:0.1	60	80	45	95
5	500:1:0.1	90	95	46	95

* Reaction period 90 minutes; Conversions were calculated using ^{1}H NMR.

Table S3. Xanthate and dithiocarbamate RAFT agents used for the synthesis of high molar mass VAc polymers

Sr. No.	RAFT agent	Molar mass (Da)	*Đ*	Time	Ref
1		80200	2.6	6 h	32
`2		50000	2.0	4.25 h	23
3		6700	1.40	4.5 h	35
4		27690	1.46	16 h	36
5		129210	1.54	1 h	31
##6		66360	1.40	1.5 h	##
7		132970	1.31	1.5 h	Present work

VAc was polymerized using morpholine based CTA (used in ref.31) with a MON:CTA:Initiator ratio of 4000:1:0.5 same as that of the present work reported in entry 7, to have a clear cut comparison.

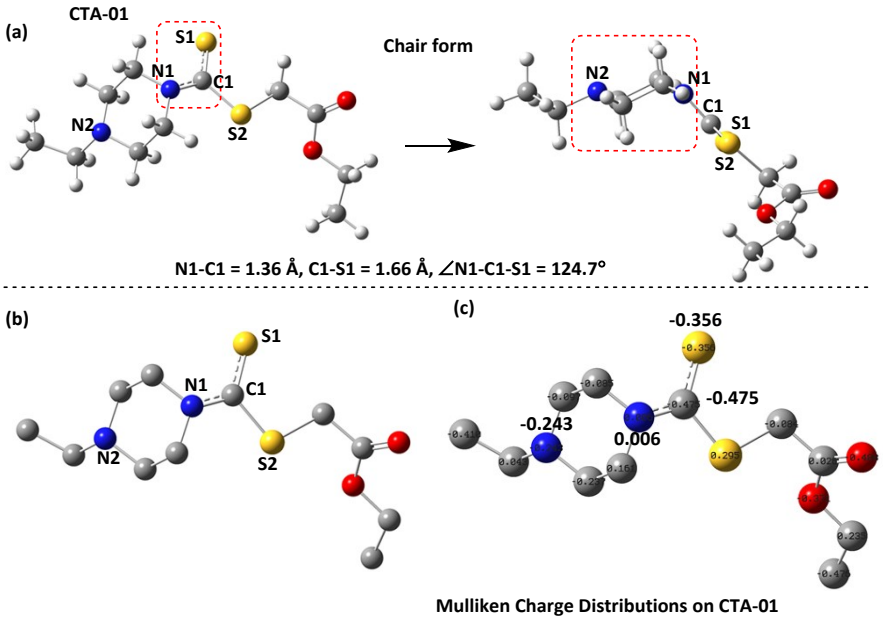


Figure S1. Optimized geometry of compound 1 (chair form) at MP2/g-31++(d,p) level of theory: (a) Front view and side view of chair from of CTA-01, (b) Front view of CTA-01 without hydrogen atoms and (c) Mulliken charges on all atoms of CTA-01.

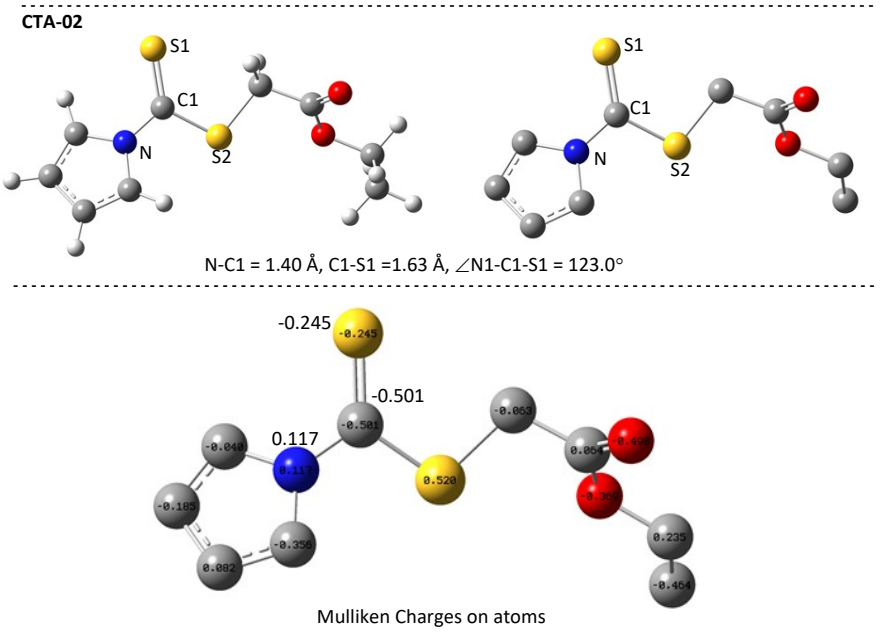
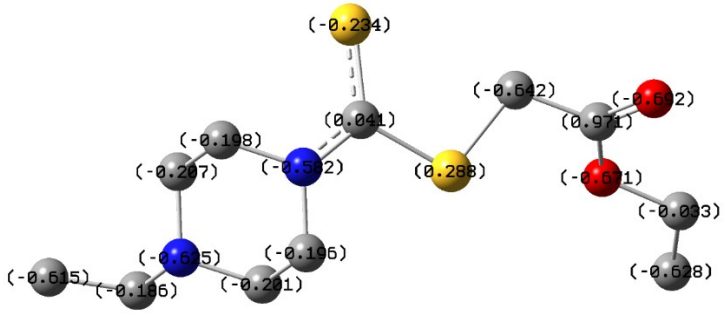
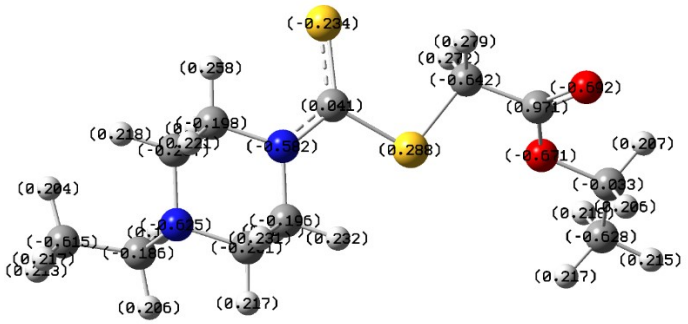


Figure S2. Optimized geometry of CTA-02 at MP2/g-31++(d,p) level of theory: (a) Front view of with hydrogen, (b) Front without hydrogen atoms and (c) Mulliken charges on all atoms of CTA-02.

(a)

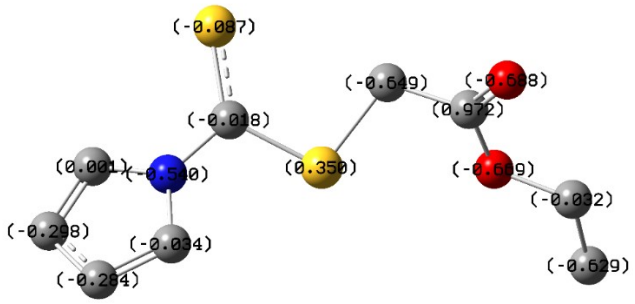


(i)

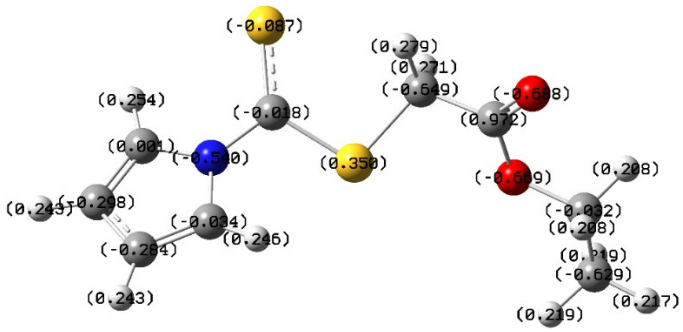


(ii)

(b)



(iii)



(iv)

Figure S3. (a) CTA-01 NPA charges (i) without hydrogen (H-atoms are hide) and (ii) with hydrogen. (b) CTA-02 NPA charges (iii) without hydrogen (H-atoms are hide) and (iv) with hydrogen.

Table S4. Stable form CTAs and energies of the CTAs

CTA	Stable form	Methods	Energy (Kcal/mol)
CTA-01	zwitterionic form	b3lyp/6-31++(d,p)	-933321.2159596899
		mp2/6-31++(d,p)	-931310.1876005945
CTA-02	Neutral	b3lyp/6-31++(d,p)	-847791.2616815767
		mp2/6-31++(d,p)	-846068.2388972407

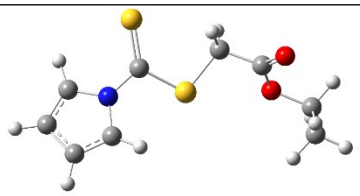
Optimized Geometries of CTA-01 and CTA-02 Energies and Their Coordinates

CTA-01	Energy (Hartree)
Electronic Energy (EE)	-1484.404619
Zero-point Energy Correction	0.319093
Thermal Free Energy Correction	0.267691
EE + Thermal Free Energy Correction	-1484.136929

Coordinates of the optimized geometry of CTA-01

0	1	X	Y	Z
C		-1.79796	-0.19403	0.249934
C		-1.05743	-1.3934	-0.32367
N		0.005224	-0.91722	-1.21032
C		-0.55919	-0.12805	-2.30673
C		-1.299	1.069852	-1.72642
N		-2.36489	0.616022	-0.83217
H		-2.60541	-0.5496	0.89015
H		-0.61628	-2.00063	0.461152
H		0.217702	0.181795	-3.00138
H		-0.57263	1.717715	-1.20334
H		-1.09887	0.394383	0.870841
H		-1.74011	-2.00167	-0.92178
H		-1.26123	-0.76852	-2.84621
H		-1.75049	1.64866	-2.5359
C		-3.11123	1.768282	-0.31569
H		-2.46989	2.388656	0.334724
H		-3.37933	2.379108	-1.18052
C		-4.37894	1.369736	0.425742
H		-4.16624	0.879557	1.374369
H		-4.97068	2.259272	0.643843
H		-4.97529	0.697105	-0.19028
C		1.286702	-0.8009	-0.76059
S		1.845355	-1.42902	0.668253
C		3.953512	-0.11311	-1.09311
H		3.96424	0.400389	-0.13211
H		4.161203	-1.16955	-0.95206

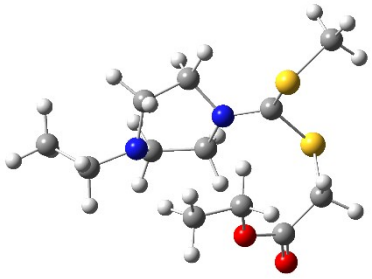
S	2.338819	0.109788	-1.88453
C	5.011951	0.466278	-2.00369
O	5.947935	-0.16494	-2.47209
O	4.801836	1.787304	-2.21372
C	5.777818	2.4388	-3.07171
H	6.763763	2.319467	-2.62308
H	5.776457	1.934811	-4.03794
C	5.363774	3.886966	-3.17556
H	5.356316	4.354782	-2.19267
H	6.069418	4.423179	-3.81045
H	4.370159	3.971462	-3.61219



CTA-02	Energy (Hartree)
Electronic Energy (EE)	-1348.442668
Zero-point Energy Correction	0.192928
Thermal Free Energy Correction	0.147395
EE + Thermal Free Energy Correction	-1348.295273

Coordinates of the optimized geometry of CTA-02

0	1	X	Y	Z
	C	1.424189	-0.61297	-0.90817
	S	1.91017	-2.05379	-0.30787
	C	3.971638	-0.38056	-1.90697
	H	4.469989	-0.52365	-0.94772
	H	3.72915	-1.34658	-2.34243
	S	2.458899	0.590136	-1.66991
	C	4.882445	0.361981	-2.85791
	O	5.357751	-0.11541	-3.87689
	O	5.11825	1.617578	-2.41464
	C	5.990596	2.420566	-3.25951
	H	6.950348	1.9111	-3.34029
	H	5.545398	2.478008	-4.25231
	C	6.107575	3.772565	-2.59872
	H	6.536497	3.67709	-1.60287
	H	6.755702	4.413915	-3.19615
	H	5.130784	4.2459	-2.51703
	N	0.101822	-0.14678	-0.81648
	C	-0.79883	-0.52911	0.172998
	C	-0.51695	0.775424	-1.66152
	C	-1.9757	0.149154	-0.04543
	H	-0.50209	-1.22738	0.935565
	C	-1.80097	0.966581	-1.20351
	H	-0.0129	1.155272	-2.53306
	H	-2.85904	0.076343	0.56839
	H	-2.53753	1.604487	-1.66521

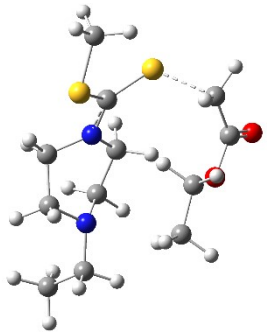


CTA-01a	Energy (Hartree)
Electronic Energy (EE)	-1524.102686
Zero-point Energy Correction	0.356722
Thermal Free Energy Correction	0.304614
EE + Thermal Free Energy Correction	-1523.798071

Coordinates of the optimized geometry of CTA-01a

0	2	X	Y	Z
C		5.456916	1.136317	-1.38941
S		6.218908	-0.04852	-2.46629
S		6.192465	2.712762	-1.21778
C		7.71422	-0.40635	-1.50808
H		8.336771	-1.05747	-2.12046
H		8.25303	0.516078	-1.30247
H		7.464728	-0.90962	-0.57643
C		6.039486	3.469838	-2.89621
H		6.286741	2.71157	-3.63659
H		6.790855	4.258633	-2.91841
C		4.695849	4.137089	-3.09227
O		4.453331	5.243609	-2.63306
O		3.703154	3.469315	-3.74136
C		3.954155	2.202442	-4.40403
H		4.305926	1.475031	-3.67584
H		4.711017	2.347951	-5.17805
C		2.634609	1.767152	-4.99612
H		2.771037	0.828253	-5.53548
H		1.914679	1.61647	-4.19352
H		2.260001	2.518428	-5.69024
C		3.289291	2.07815	-0.627
H		3.647368	2.344605	0.37532
C		2.203372	-0.47853	-1.65589
H		1.596815	-1.23379	-1.13212
N		4.094359	0.987266	-1.19372
N		1.542102	0.824333	-1.74937
C		1.821182	1.639513	-0.57645
C		3.524787	-0.32629	-0.9007

H	1.597318	1.123265	0.371037
H	3.36848	-0.40755	0.182849
H	2.38811	-0.8415	-2.67193
H	3.379751	2.950252	-1.26903
H	1.193144	2.532177	-0.61123
H	4.229151	-1.09883	-1.19577
C	0.126669	0.739144	-2.10862
H	-0.19175	1.744039	-2.40122
H	0.065933	0.111478	-3.00268
C	-0.82032	0.199952	-1.03335
H	-0.82831	0.845043	-0.15466
H	-1.83718	0.159927	-1.42648
H	-0.54654	-0.80679	-0.71766

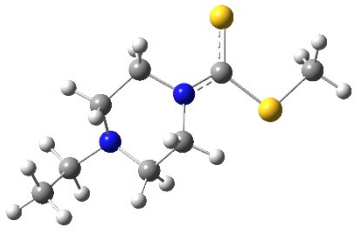


*CTA-01b (TS)	Energy (Hartree)
Electronic Energy (EE)	-1524.078734
Zero-point Energy Correction	0.354192
Thermal Free Energy Correction	0.302888
EE + Thermal Free Energy Correction	-1523.775846
Imaginary Frequency	-625.84 cm^{-1}

Coordinates of the optimized geometry of *CTA-01b

0	2	X	Y	Z
C		5.361206	0.936463	-1.2096
S		6.119224	-0.51052	-1.96176
S		6.179026	2.416471	-1.07648
C		7.900091	-0.20376	-1.72515
H		8.39382	-1.1024	-2.1036
H		8.229555	0.668483	-2.28905
H		8.131183	-0.0714	-0.66703
C		6.173177	3.549214	-3.00908
H		6.479497	2.791817	-3.72213
H		6.956041	4.247033	-2.72946
C		4.86375	4.197479	-3.15597
O		4.588485	5.27193	-2.64555
O		3.862182	3.536262	-3.81946
C		4.11947	2.354442	-4.60323
H		4.569769	1.574912	-3.97925
H		4.818621	2.601902	-5.41261
C		2.787394	1.884915	-5.16142
H		2.938765	0.997879	-5.78646
H		2.106272	1.627635	-4.34484
H		2.326255	2.66651	-5.77242
C		3.223443	1.979252	-0.53403
H		3.558486	2.37119	0.435871
C		2.062842	-0.59025	-1.47932
H		1.430528	-1.34191	-0.97275
N		4.032686	0.804255	-0.91533
N		1.417758	0.718245	-1.59757
C		1.732719	1.603852	-0.48418

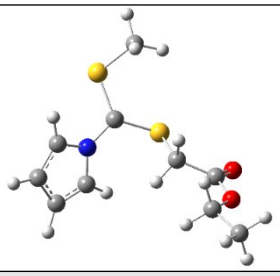
C	3.362524	-0.47516	-0.6664
H	1.466928	1.178843	0.501956
H	3.138925	-0.53376	0.408331
H	2.273498	-0.96929	-2.48801
H	3.378185	2.757964	-1.28125
H	1.154016	2.52645	-0.59197
H	4.031477	-1.30189	-0.89724
C	0.015658	0.677098	-2.01099
H	-0.26548	1.692613	-2.31662
H	-0.03663	0.055361	-2.91413
C	-1.00125	0.161364	-0.97615
H	-1.02486	0.795611	-0.08351
H	-2.00709	0.164428	-1.41029
H	-0.78377	-0.86367	-0.65758



CTA-01c	Energy (Hartree)
Electronic Energy (EE)	-1217.932395
Zero-point Energy Correction	0.245722
Thermal Free Energy Correction	0.203999
EE + Thermal Free Energy Correction	-1217.728396

Coordinates of the optimized geometry of CTA-01c

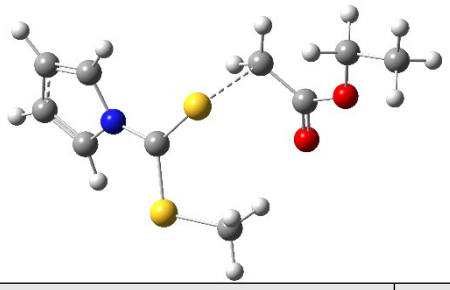
0	1	X	Y	Z
C		5.373474	0.883776	-1.03882
S		6.129118	-0.63923	-1.58951
S		6.173935	2.335654	-1.02373
C		7.803002	-0.0978	-1.97004
H		8.322392	-0.99962	-2.29276
H		7.802865	0.638849	-2.76795
H		8.28717	0.315307	-1.08967
C		3.284895	1.92874	-0.31846
H		3.535679	2.29063	0.684829
C		2.193283	-0.53054	-1.55566
H		1.458607	-1.26963	-1.20004
N		4.082703	0.742709	-0.64688
N		1.636901	0.818273	-1.67825
C		1.802106	1.586458	-0.4527
C		3.350745	-0.51523	-0.55555
H		1.418777	1.076232	0.445551
H		2.972975	-0.60586	0.467087
H		2.544549	-0.85053	-2.54021
H		3.543868	2.707344	-1.03474
H		1.244076	2.52031	-0.549
H		4.016021	-1.35798	-0.71998
C		0.289923	0.845768	-2.24688
H		0.084623	1.878771	-2.54063
H		0.324722	0.255439	-3.16641
C		-0.83803	0.339484	-1.34433
H		-0.93171	0.952922	-0.44795
H		-1.78761	0.384638	-1.87951
H		-0.67954	-0.69423	-1.03699



CTA-02a	Energy (Hartree)
Electronic Energy (EE)	-1388.155557
Zero-point Energy Correction	0.233066
Thermal Free Energy Correction	0.184861
EE + Thermal Free Energy Correction	-1387.970696

Coordinates of the optimized geometry of CTA-02a

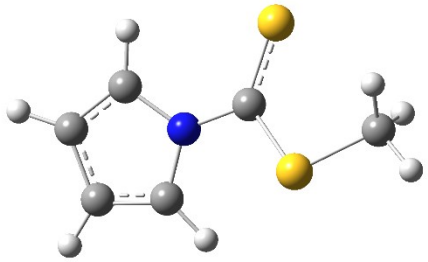
0	2	X	Y	Z
C		5.496189	0.879811	-1.06683
S		6.658849	-0.18941	-0.29348
S		5.912722	2.541946	-1.42223
C		8.082541	-0.12492	-1.44447
H		8.883326	-0.69073	-0.96266
H		7.829074	-0.58948	-2.3999
H		8.406547	0.906025	-1.59434
C		5.22611	2.668076	-3.13132
H		4.169072	2.385524	-3.11744
H		5.752635	1.966068	-3.78626
C		5.39811	4.088508	-3.64666
O		5.985944	4.949903	-3.035
O		4.872416	4.377573	-4.86157
C		4.12498	3.410846	-5.63661
H		3.227251	3.114321	-5.0823
H		4.74082	2.521075	-5.81065
C		3.755551	4.077354	-6.94906
H		3.181292	3.380484	-7.56828
H		3.146883	4.968362	-6.77199
H		4.653006	4.374219	-7.49887
C		3.660084	-0.7928	-1.23008
C		3.058548	1.330664	-0.75333
C		2.288995	-0.76387	-1.13445
H		4.343457	-1.59929	-1.44272
C		1.907667	0.580329	-0.83184
H		3.217834	2.369993	-0.51228
H		1.631293	-1.61193	-1.26483
H		0.90451	0.951017	-0.67304
N		4.143469	0.49326	-0.99722



*CTA-02b (TS)	Energy (Hartree)
Electronic Energy (EE)	-1388.120027
Zero-point Energy Correction	0.234275
Thermal Free Energy Correction	0.188575
EE + Thermal Free Energy Correction	-1387.931452
Imaginary Frequency	-389.11 cm^{-1}

Coordinates of the optimized geometry of *CTA-02b (TS)

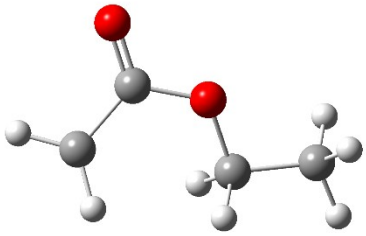
0	2	X	Y	Z
C		4.5976	0.734551	-1.33645
S		6.195919	0.499021	-0.63487
S		4.054869	2.158026	-2.03267
C		7.124149	1.969055	-1.17515
H		8.114635	1.844803	-0.73035
H		7.202399	1.989681	-2.26355
H		6.657539	2.879097	-0.79749
C		4.345973	1.872276	-4.46239
H		3.445452	2.40067	-4.7489
H		4.296225	0.791021	-4.45776
C		5.675735	2.429439	-4.68048
O		6.695409	1.757538	-4.57917
O		5.816752	3.758164	-4.95891
C		4.67705	4.626761	-5.10712
H		4.075652	4.608832	-4.19033
H		4.055685	4.279063	-5.94208
C		5.204226	6.025083	-5.37709
H		4.367286	6.720105	-5.50285
H		5.82284	6.372339	-4.54459
H		5.810084	6.040592	-6.28757
C		4.215691	-1.72317	-1.04622
C		2.395958	-0.40906	-1.37279
C		3.110602	-2.52867	-1.01824
H		5.263842	-1.96319	-0.97531
C		1.958253	-1.69508	-1.21939
H		1.865111	0.515366	-1.52661
H		3.119767	-3.60134	-0.88467
H		0.925676	-2.01381	-1.24492
N		3.792034	-0.40524	-1.26609



CTA-02c	**Energy (Hartree)**
Electronic Energy (EE)	-1081.982372
Zero-point Energy Correction	0.119940
Thermal Free Energy Correction	0.084639
EE + Thermal Free Energy Correction	-1081.897733

Coordinates of the optimized geometry of CTA-02c

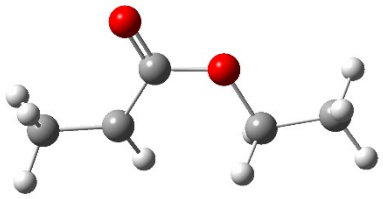
0	**1**	**X**	**Y**	**Z**
C		5.666898	0.920033	-1.05121
S		6.543742	-0.60112	-1.00198
S		6.306892	2.402356	-0.79397
C		8.246588	-0.02725	-0.89997
H		8.858954	-0.92692	-0.93093
H		8.487817	0.614557	-1.74404
H		8.419493	0.508627	0.029263
C		3.735932	-0.36352	-1.99444
C		3.282315	1.557033	-0.87813
C		2.370505	-0.1871	-2.00107
H		4.35394	-1.11167	-2.45917
C		2.085524	1.020287	-1.29392
H		3.515337	2.442549	-0.3137
H		1.660873	-0.84218	-2.48057
H		1.112588	1.440422	-1.09569
N		4.299785	0.710947	-1.3071



P1	**Energy (Hartree)**
Electronic Energy (EE)	-306.147158
Zero-point Energy Correction	0.107541
Thermal Free Energy Correction	0.075760
EE + Thermal Free Energy Correction	-306.071398

Coordinates of the optimized geometry of P1

0	**2**	**X**	**Y**	**Z**
C		6.037298	3.562235	-3.12969
H		6.415991	2.917957	-3.90529
H		6.696447	3.905548	-2.35043
C		4.693261	4.185277	-3.17605
O		4.449091	5.231409	-2.62337
O		3.725395	3.548768	-3.88283
C		3.959318	2.233958	-4.44275
H		4.361883	1.575901	-3.67121
H		4.678331	2.31193	-5.26074
C		2.622934	1.737519	-4.94314
H		2.742788	0.750462	-5.39011
H		1.913202	1.66795	-4.12148
H		2.224901	2.416868	-5.69407



P2	Energy (Hartree)
Electronic Energy (EE)	-345.338683
Zero-point Energy Correction	0.136772
Thermal Free Energy Correction	0.102251
EE + Thermal Free Energy Correction	-345.236431

Coordinates of the optimized geometry of P2

0	2	X	Y	Z
C		3.371507	3.078052	-4.38385
H		3.667287	2.215251	-4.96055
C		3.955439	4.409958	-4.65589
O		3.435718	5.435996	-4.2722
O		5.110355	4.471289	-5.37086
C		5.836975	3.270592	-5.72128
H		5.25854	2.692065	-6.44464
H		5.998846	2.667717	-4.82615
C		7.14855	3.72409	-6.31958
H		7.737356	2.855238	-6.61463
H		6.969386	4.341394	-7.19756
H		7.71533	4.303396	-5.59362
C		2.224743	2.98921	-3.4467
H		2.121446	1.981051	-3.04942
H		2.339298	3.702911	-2.63318
H		1.291685	3.246494	-3.95946

Table S5. Energies details of reactants, transition states and products calculated at MP2/6-31++(d,p) in Hartree.

	CTA-01a	*CTA-01b	CTA-01c	CTA-02a	*CTA-02b	CTA-02c	P1
E_0	-1524.102686	-1524.078734	-1217.932395	-1388.155557	-1388.120027	-1081.982372	-306.147158
E_{ZPE}	0.356722	0.354192	0.245722	0.233066	0.234275	0.119940	0.107541
E_{tot}	0.377966	0.374912	0.259305	0.249993	0.249991	0.129134	0.114753
H_{corr}	0.378911	0.375856	0.260249	0.250937	0.250935	0.130078	0.115697
G_{corr}	0.304614	0.302888	0.203999	0.184861	0.188575	0.084639	0.075760
$E_0 + E_{ZPE}$	-1523.745964	-1523.724542	-1217.686673	-1387.922491	-1387.885751	-1081.862432	-306.039617
$E_0 + E_{tot}$	-1523.724719	-1523.703822	-1217.673090	-1387.905564	-1387.870036	-1081.853238	-306.032406
$E_0 + H_{corr}$	-1523.723775	-1523.702878	-1217.672145	-1387.904620	-1387.869092	-1081.852294	-306.031461
$E_0 + G_{corr}$	-1523.798071	-1523.775846	-1217.728396	-1387.970696	-1387.931452	-1081.897733	-306.071398

*Energies barrier (in Kcal/mol)					
	*CTA-01b	*CTA-02b			
ΔG	13.946401	24.6259871	*Transition state (TS)		

Table S6. Energies details of reactants, transition states and products calculated at B3LYP/6-31++(d,p) in Hartree.

	CTA-01a	*CTA-01b	CTA-01c	CTA-02a	*CTA-02b	CTA-02c	P1
E0	-1527.4383	-1527.43804	-1220.387746	-1391.043500	-1391.039902	-1083.983092	-307.053454
E_{ZPE}	0.348990	0.346447	0.240487	0.226844	0.224969	0.118714	0.103691
E_{tot}	0.373216	0.373959	0.255596	0.245137	0.246525	0.129563	0.111310
H_{corr}	0.374303	0.375046	0.256682	0.246224	0.247612	0.130650	0.112397
G_{corr}	0.287211	0.280859	0.193127	0.173662	0.164680	0.076697	0.067694

$E_0 + E_{ZPE}$	-1527.08936	-1527.09160	-1220.147260	-1390.816656	-1390.814933	-1083.864377	-306.949762
$E_0 + E_{tot}$	-1527.06513	-1527.06408	-1220.132151	-1390.798363	-1390.793376	-1083.853528	-306.942144
$E_0 + H_{corr}$	-1527.06405	-1527.06300	-1220.131064	-1390.797276	-1390.792289	-1083.852442	-306.941057
$E_0 + G_{corr}$	-1527.15114	-1527.15719	-1220.194619	-1390.869838	-1390.875222	-1083.906394	-306.985760
***Energies barrier (in Kcal/mol)**							
	***CTA-01b**	***CTA-02b**					
ΔG	-3.796433	-3.37851173		*Transition state (TS)			